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REDUCTION OF HALOGENATED ETHANES BY GREEN RUST

Edward J. O'Loughlin*†‡ and David R. Burris†§
†Air Force Research Laboratory, AFRL/MLQR, Tyndall AFB, Florida 32403-5301, USA
‡Environmental Research Division, Argonne National Laboratory, Argonne, Illinois 60439-4843, USA
§Integrated Science and Technology, 433 Harrison Avenue, Panama City, Florida 32401, USA

Abstract—Green rusts, mixed Fe^{II}/Fe^{III} hydroxide minerals present in many suboxic environments, have been shown to reduce a number of organic and inorganic contaminants. The reduction of halogenated ethanes was examined in aqueous suspensions of green rust, both alone and with the addition of Ag^I (AgGR) and Cu^{II} (CuGR). Hexachloroethane (HCA), pentachloroethane (PCA), 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA), 1,1-dichloroethane (1,1-DCA), and 1,2-dibromoethane were reduced in the presence of green rust alone, AgGR, or CuGR; only 1,2-dichloroethane and chloroethane were nonreactive. The reduction was generally more rapid for more highly substituted ethanes than for ethanes having fewer halogen groups (HCA > PCA > 1,1,1,2-TeCA > 1,1,1-TCA > 1,1,2,2-TeCA > 1,1,2-TCA > 1,1-DCA), and isomers with the more asymmetric distributions of halogen groups were more rapidly reduced than the isomer with greater symmetry (e.g., 1,1,1-TCA > 1,1,2-TCA). The addition of Ag^I or Cu^{II} to green rust suspensions resulted in a substantial increase in the rate of halogenated ethane reduction as well as significant differences in the product distributions with respect to green rust alone.

Keywords—Fe(II)-Fe(III) hydroxide   Reductive dehalogenation   Chlorinated ethanes   Chlorinated hydrocarbons   Ethylene dibromide

INTRODUCTION

Many studies have shown that Fe^{II} can reduce a range of organic and inorganic contaminants [1–21], and Fe^{II} is one of the most abundant reductants typically present in aquatic and terrestrial environments under suboxic and anoxic conditions [22–24]. In these environments, Fe^{II} may be present as soluble organic and inorganic complexes, as surface complexes, and as a host of Fe^{II}-bearing mineral phases. Although aqueous Fe^{II} complexes can reduce a number of contaminants [1,15], Fe^{II} complexed with mineral surfaces and structural Fe^{II} in Fe^{II}-bearing minerals are often more powerful reductants [25]. Indeed, contaminants such as carbon tetrachloride (CT), nitrobenzenes, and U^{VI} are readily reduced by sorbed or structural Fe^{II} but not by aqueous Fe^{II} complexes [3,8,9].

A number of Fe^{II}-bearing minerals may be present in soils and sediments under suboxic and anoxic conditions, including Fe^{II}-containing clays (e.g., smectites, vermiculites, and micas), ilmenite, magnetite, siderite, vivianite, iron sulfide, pyrite, and green rust, and many of these have been reported to reduce a number of contaminants. Several clay minerals containing structural Fe^{II} have been shown to reduce chlorinated hydrocarbons [12,14], nitroaromatics [17], pesticides [10], and Cr^{VI} [11]. Magnetite can reduce CT [19] as well as Cr^{VI}, Cu^{II}, and V^V [4,5]. Among the most versatile Fe^{II}-bearing mineral reductants are green rusts, which have been reported to reduce CT [7,26]; chlorinated ethenes [18]; and a suite of inorganic contaminants, including nitrate and nitrite, Ag^I, Au^{III}, Cr^{VI}, Cu^{II}, Hg^{II}, Se^{VI}, and U^{VI} [2,6,13,16,20,21].

Green rusts are mixed Fe^{II}/Fe^{III} hydroxides that have layered structures consisting of alternating positively charged hydrox-ide layers and hydrated anion layers with the following general composition:

$$[Fe^{II}_{(6-x)}Fe^{III}_x(OH)_{12}]^{x+}[(A)_{x/n}yH_2O]^{x-}$$
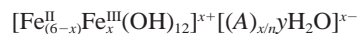
where $x = 0.9$ to 4.2, A is a n-valent anion (typically Cl^-, SO_4^{2-}, or CO_3^{2-}; however, green rusts containing Br^-, I^-, NO_3^-, ClO_4^-, SO_3^{2-}, SeO_4^{2-}, and oxalate have been prepared), and y denotes the varying amounts of interlayer water ($y = 2$–4 for most green rusts). Green rusts typically form under circumneutral to alkaline conditions in suboxic environments and have been identified as products of both abiotic and microbially induced corrosion of iron and steel [27,28], the abiotic reductive dissolution of Fe^{III} oxyhydroxides by Fe^{2+} [29], dissimilatory iron reduction [30,31], and microbial bio-oxidation of Fe^{II} [32]. In addition, green rusts are metastable intermediates in the transformation of Fe^{II} to magnetite and Fe^{III} oxyhydroxides (e.g., lepidocrocite and goethite) under near-neutral to alkaline conditions, and they are believed to play a central role in the redox cycling of iron in many aquatic and terrestrial environments.

Because of the widespread use of halogenated ethanes as solvents, feedstocks for industrial-scale chemical synthesis, pesticides, pharmaceuticals, fuel additives, refrigerants, and propellants, these compounds constitute an important and widely recognized class of environmental contaminants. Under suboxic and anoxic conditions, halogen groups may be removed from halogenated ethanes by reductive dehalogenation reactions, resulting in products that, ideally, are of less concern than the parent compounds, although this is not always the case. The present study examined the reduction of a series of halogenated ethanes by green rust, both alone and with the addition of Ag^I and Cu^{II}, which have been shown to enhance the reduction of chlorinated methanes by green rust [26].

* To whom correspondence may be addressed
(oloughlin@anl.gov).

MATERIALS AND METHODS

Chemicals

Hexachloroethane (HCA; 98%), pentachloroethane (PCA; 95%), 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA; 99%), 1,2-dichloroethane (1,2-DCA; 99.8%), 1,2-dibromoethane (ethylene dibromide [EDB]; 99%), bromoethane (99+%), tetrachloroethene (perchloroethene [PCE]; 99.9+%), trichloroethene (TCE; 99.9+%), 1,1-dichloroethene (1,1-DCE; 99%), *cis*-1,2-dichloroethene (*cis*-1,2-DCE; 97%), *trans*-1,2-dichloroethene (*trans*-1,2-DCE; 98%), iron(II) sulfate heptahydrate (99+%), copper(II) chloride (99.999%), silver(I) acetate (99.999%), propene (99+%), *n*-heptane (99+%), 1-butene (99+%), and a mixture of *cis*- and *trans*-2-butene (38.1% *cis* and 61.6% *trans*) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Chloroethane (CA; 99%), 1,1-dichloroethane (1,1-DCA; 99%), 1,1,1-trichloroethane (1,1,1-TCA; 100%), 1,1,2-trichloroethane (1,1,2-TCA; 99.8%), and 1,1,1,2-tetrachloroethane (1,1,1,2-TeCA; 99%) were purchased from Chem Service (West Chester, PA, USA). A multicomponent gas mixture containing methane, ethane, ethene, and acetylene (each at 1.0 mol% in N_2) along with propane (mol% in N_2), *n*-butane (mol% in N_2), and chloroethene (vinyl chloride [VC]; mol% in N_2) were purchased from Scott Specialty Gases (Plumsteadville, PA, USA).

Green rust in which the interlayer anion is SO_4^{2-} (GR_{SO_4}) was synthesized by air oxidation of a 1.0 M ferrous sulfate solution. Briefly, 278 g of $FeSO_4 \cdot 7H_2O$ were dissolved in 1 L of distilled, deionized water on a magnetic stirrer under ambient atmosphere. On dissolution, 1.0 M NaOH was added dropwise until the pH remained stable at 7.0, at which point the GR_{SO_4} suspension was placed in an anoxic glove box (4–6% H_2 in N_2). The GR_{SO_4} was recovered by centrifugation and subsequently washed four times with distilled, deionized water.

Experimental setup

The reaction system consisted of 160-ml serum vials crimp-sealed with Teflon®-lined rubber septa. Each vial contained 94 ml of distilled, deionized water; 5 ml of GR_{SO_4} suspension (~0.5 g of GR_{SO_4}); either 1 ml of 0.1 M HCl, 1 ml of 10^{-2} M Ag^I, or 1 ml of 10^{-2} M Cu^{II} in 0.1 M HCl; and 0.1 ml of 1.0 M NaOH (for the systems containing green rust alone or green rust with Cu^{II}). All preparative work was performed in an anoxic glove box. The vials were sealed and spiked with 5 µmol of *n*-heptane (5 µl of a 1.0 M methanolic solution of *n*-heptane) used as an internal standard. Reduction reactions were initiated by spiking with 2 µmol of a given halogenated ethane (20 µl of 0.1 M methanolic solutions of either HCA or PCA, or 2 µl of 1.0 M methanolic solutions of all other halogenated ethanes). Initial solution concentrations were 5 mg ml⁻¹ for GR_{SO_4} and 100 µM for Ag^I or Cu^{II} (except for controls containing green rust only); the total mass of halogenated ethane in each vial was 2 µmol. The vials were placed on a roller drum (rotating vertically as the bottle axis remained horizontal) in an incubator maintained at 20°C. For reactions with fast kinetics (reaction complete in <15 min), the vials were vigorously shaken by hand under ambient conditions.

At selected intervals, 200-µl headspace samples were removed from the serum vials for analysis using a Hewlett-Packard 5890 Series II gas chromatograph (Avondale, PA, USA). Hexachloroethane, PCA, 1,1,1,2-TeCA, 1,1,2,2-TeCA, and EDB were analyzed with a DB-1 column (inner diameter, 0.53 mm; length, 30 m) (J&W Scientific, Folsom, CA, USA)

and a flame ionization detector (200°C). Samples were injected in split mode (split ratio, 2:1) at 200°C with helium as the carrier gas. The oven temperature for EDB was held at 50°C for 1 min, ramped at 25°C min⁻¹ to 100°C, and held at 100°C for 1 min. For 1,1,1,2-TeCA and 1,1,2,2-TeCA, the oven temperature was held at 60°C for 1.2 min, ramped at 30°C min⁻¹ to 100°C, and held at 100°C for 2.5 min. For PCA, the oven temperature was held at 60°C for 1 min, ramped at 30°C min⁻¹ to 150°C, and held at 150°C for 1 min. For HCA, the oven temperature was ramped from 90°C to 180°C at 30°C min⁻¹ and then held at 180°C for 1 min. All other hydrocarbons were analyzed with a GSQ column (inner diameter, 0.53 mm; length, 30 m) (J&W Scientific) and a flame ionization detector (240°C). Samples were injected in split mode (split ratio, 2:1) at 180°C with helium as the carrier gas. The oven temperature was held at 50°C for 2 min, ramped at 25°C min⁻¹ to 200°C, and held at 200°C for 10 min. Both systems were calibrated by equilibrating known masses of analytes and internal standard (*n*-heptane) in serum vials containing the same ratio of aqueous phase to vapor phase as the experimental systems, thus accounting for water-vapor partitioning. Vapor–liquid partitioning in these systems was rapid relative to the reaction kinetics.

RESULTS AND DISCUSSION

Reduction of chlorinated ethanes

Nearly all the halogenated ethanes examined in the present study were partially or fully reduced in the presence of green rust (Fig. 1); only CA and 1,2-DCA were nonreactive (data not shown). Moreover, the addition of Ag^I or Cu^{II} to green rust suspensions (henceforth, designated AgGR and CuGR) resulted in a significant increase in the rate of reduction of halogenated ethanes as compared to green rust alone (Fig. 1). The effectiveness of green rust as a reductant for halogenated ethanes was clearly related to the number and distribution of halogen substituents. Reduction was generally more rapid for more highly substituted ethanes than for ethanes having fewer halogen groups, such that HCA > PCA > 1,1,1,2-TeCA > 1,1,1-TCA > 1,1,2,2-TeCA > 1,1,2-TCA > 1,1-DCA. In the case of structural isomers, the isomer with the more asymmetric distribution of halogen groups was reduced by green rust more rapidly than the isomer with greater symmetry (e.g., 1,1,1-TCA was more readily reduced than 1,1,2-TCA). In addition, the nature of the halogen groups had a significant effect on the extent of reduction, and although 1,2-DCA was not reduced by green rust, EDB (the brominated analogue of 1,2-DCA) was readily reduced.

As previously mentioned, CA and 1,2-DCA were not reduced in the presence of green rust alone, AgGR, or CuGR (Table 1). However, 25% of EDB, the brominated analogue of 1,2-DCA, was reduced by green rust within 10 d, whereas EDB was completely reduced by AgGR or CuGR within 2 or 70 min, respectively. The reductive dehalogenation of halogenated ethanes can occur via a number of reaction types, including hydrogenolysis, α-elimination, β-elimination (for vicinal halides only), coupling, and dehydrohalogenation; the last reaction, although overall not a reduction reaction, does involve an electron transfer as the initial step. In the case of EDB, reductive dehalogenation may occur by reductive β-elimination, hydrogenolysis, and dehydrohalogenation, resulting in ethene (which may be further reduced to ethane), bromoethane (which may be further reduced to ethane), and vinyl bromide (which may be subsequently reduced to ethene and
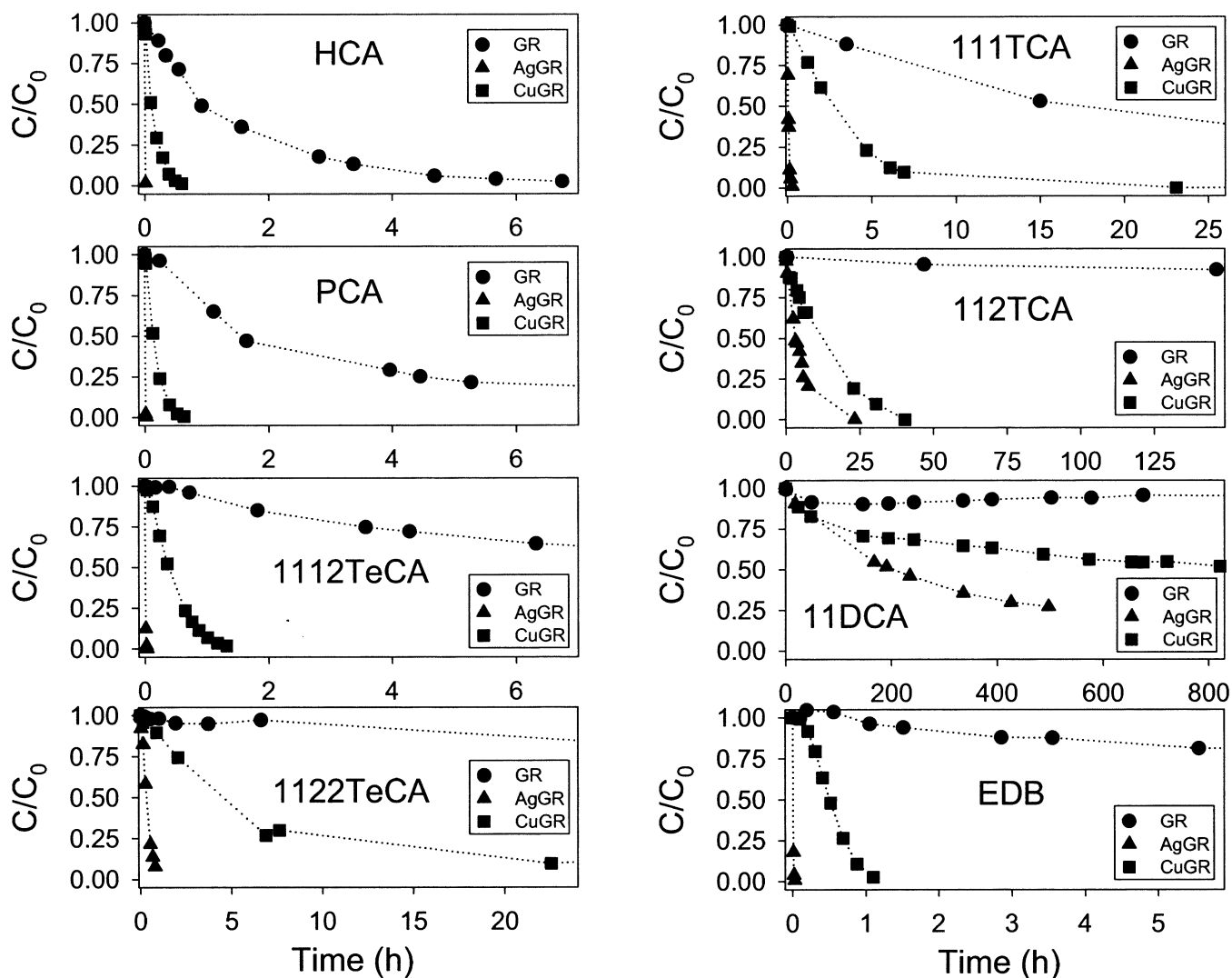
Fig. 1. Reduction of halogenated ethanes in aqueous suspensions containing 2 μmol of the indicated halogenated ethane and 0.5 g of hydroxysulfate green rust (GR) either without or with the addition 10 μmol of Ag^I (AgGR) or Cu^{II} (CuGR). Lines are for visualization purposes only. HCA = hexachloroethane; PCA = pentachloroethane; 1,1,1,2-TeCA = 1,1,1,2-tetrachloroethane; 1,1,2,2-TeCA = 1,1,2,2-tetrachloroethane; 1,1,1-TCA = 1,1,1-trichloroethane; 1,1,2-TCA = 1,1,2-trichloroethane; 1,1-DCA = 1,1-dichloroethane; EDB = ethylene dibromide.

then ethane), respectively. Ethene was the only observed product of EDB reduction by green rust and AgGR and was the initial product of EDB reduction by CuGR, indicating that β-elimination was the only significant mechanism for EDB reduction in these systems. Further reduction of ethene to ethane was observed only in the CuGR system, a result that is consistent with those of independent experiments showing reduction of ethene to ethane by CuGR but no reduction of ethene by AgGR or green rust alone.

The reduction of 1,1-DCA by green rust was minimal; after 49 d, 95% of the 1,1-DCA remained (Table 1). However, 1,1-DCA reduction was substantially enhanced with AgGR or CuGR (Fig. 1), with only 22% of 1,1-DCA remaining in the AgGR system and 53% remaining in the CuGR system after 49 d (Table 1). The principal products of 1,1-DCA reduction were CA, ethene, and ethane. Although hydrogenolysis of 1,1-DCA results in CA, CA was not reduced in any of our experimental systems; therefore, it is unlikely that the ethane produced from the reduction of 1,1-DCA was the product of sequential hydrogenolysis reactions (e.g., 1,1-DCA → CA → ethane). Ethene, which is not a product of the sequential hy-

drogenolysis of 1,1-DCA, was a significant product of 1,1-DCA reduction by green rust and CuGR and may be formed from 1,1-DCA via a reductive α-elimination reaction. A potential reaction scheme for the reduction of 1,1-DCA to ethene and ethane (without CA as an intermediate) is shown in Figure 2. The initial step in the reduction of 1,1-DCA involves a single electron transfer with the consecutive or concerted cleavage of the C–Cl bond, resulting in the formation of a chloroethane radical. This radical can accept a second electron and a proton, thus forming CA and terminating the reaction, or the radical can accept another electron with the release of a second chloride, thus forming ethanylidene (or the corresponding carbenoid). The rearrangement of this carbene results in ethene. In addition to undergoing rearrangement, the carbene might form ethane (without ethene as an intermediate) by the sequential or concerted transfer of two electrons and two protons. As previously indicated, green rust and AgGR are unable to reduce ethene; therefore, the ethane observed in these systems was probably not a product of the reduction of ethene to ethane.

The concentrations of 1,1,2-TCA were reduced below detectable levels within 23 or 40 h by AgGR or CuGR, respec-

Table 1. Initial transformation reactions and products, final product distributions, and carbon recoveries from the reductive dehalogenation of halogenated ethanes in aqueous suspensions of GR, AgGR, and CuGR[a]

Compound[b]	System	Initial transformation reaction and product[c]	Final sampling (d)	Parent compound remaining	Products[d]	Carbon recovery[e] (%)
CA	GR	NR	49	100%	NO	100
	AgGR	NR	49	98%	NO	98
	CuGR	NR	49	98%	NO	98
11DCA	GR	Uncertain	49	95%	EE(13%) & EA(19%)	96
	AgGR	Uncertain	49	22%	CA(4%), EE(<1%), & EA(92%)	97
	CuGR	Uncertain	49	53%	CA(4%), EE(15%), & EA(47%)	92
12DCA	GR	NR	49	97%	NO	97
	AgGR	NR	49	101%	NO	101
	CuGR	NR	49	102%	NO	102
EDB	GR	β-Elimination→EE	10	75%	EE(99%)	100
	AgGR	β-Elimination→EE	10	0%	EE(14%) & EA(79%)	99
	CuGR	β-Elimination→EE	10	0%	EE(14%) & EA(79%)	93
111TCA	GR	Uncertain	8	0%	11DCA(21%), CA(10%), EE(10%), & EA(19%)	60
	AgGR	Uncertain	8	0%	11DCA(3%), CA(32%), EE(1%), EA(29%), & n-butane(9%)	74
	CuGR	Uncertain	8	0%	11DCA(12%), CA(14%), EE(10%), & EA(25%)	61
112TCA	GR	β-Elimination→VC	49	94%	11DCE(19%), VC(76%), EE(3%), & EA(2%)	101
	AgGR	β-Elimination→VC	20	0%	VC(100%) & EE + EA(<1%)	100
	CuGR	β-Elimination→VC	20	0%	VC(37%), EE(42%), & EA(9%)	88
1112TeCA	GR	β-Elimination→11DCE	23	10%	11DCE(78%) & EE + EA(<1%)	88
	AgGR	β-Elimination→11DCE	12	0%	11DCE(83%), VC(<1%), & EE + EA(<1%)	83
	CuGR	β-Elimination→11DCE	12	0%	11DCE(27%), VC(1%), EE(40%), EA(10%), & C4 hydrocarbons(1%)	79
1122TeCA	GR	Dehydrochlorination→TCE	23	17%	TCE(84%), cis-1,2-DCE(2%), & trans-1,2-DCE(1%)	90
	AgGR	β-Elimination→c/t12DCE	12	0%	TCE(<1%), cis-1,2-DCE(52%), trans-1,2-DCE(31%), Ac(1%), & EE + EA(<1%)	84
	CuGR	β-Elimination→c/t12DCE	12	0%	TCE(1%), cis-1,2-DCE(33%), trans-1,2-DCE(4%), VC(1%), EE(42%), EA(8%), & C4 hydrocarbons(<1%)	89
PCA	GR	Dehydrochlorination→PCE and β-elimination→TCE	11	0%	PCE(39%) & TCE(56%)	95
	AgGR	β-Elimination→TCE	11	0%	TCE(81%), cis/trans 12DCE(1%), Ac(2%), & EE + EA(<1%)	84
	CuGR	β-Elimination→TCE	11	0%	PCE(2%), TCE(30%), EE(34%), EA(18%), & C4 hydrocarbons(1%)	85
HCA	GR	β-Elimination→PCE	11	0%	PCE(75%)	75
	AgGR	β-Elimination→PCE	11	0%	TCE(69%), cis-1,2-DCE(1%), trans-1,2-DCE(6%), Ac(9%), & EE(<1%)	85
	CuGR	β-Elimination→PCE	11	0%	PCE(47%), TCE(5%), EE(10%), & EA(4%)	66

[a] GR = green rust alone; AgGR = green rust with 10 μmol of Ag[I]; CuGR = green rust with 10 μmol Cu[II].

[b] CA = chloroethane; 11-DCA = 1,1-dichloroethane; 12-DCA = 1,2-dichloroethane; EDB = ethylene dibromide; 111TCA = 1,1,1-trichloroethane; 112-TCA = 1,1,2-trichloroethane; 1112-TeCA = 1,1,1,2-tetrachloroethane; 1122-TeCA = 1,1,2,2-tetrachloroethane; PCA = pentachloroethane; HCA = hexachloroethane.

[c] NR = No reaction (<5% loss of parent compound over course of experiment).

[d] Expressed as percent of $PC_0 - PC_f$, where PC_0 is the initial concentration of parent compound and PC_f is the final concentration. NO = none observed; EE = ethene; EA = ethane; 1,1-DCE = 1,1-dichloroethene; VC = vinyl chloride; TCE = trichloroethene; cis-1,2-DCE = cis-1,1-dichloroethene; trans-1,2-DCE = trans-1,2-dichloroethene; Ac = acetylene; PCE = perchloroethene.

[e] Carbon accounted for by identified products and any remaining parent compound, relative to PC_0.
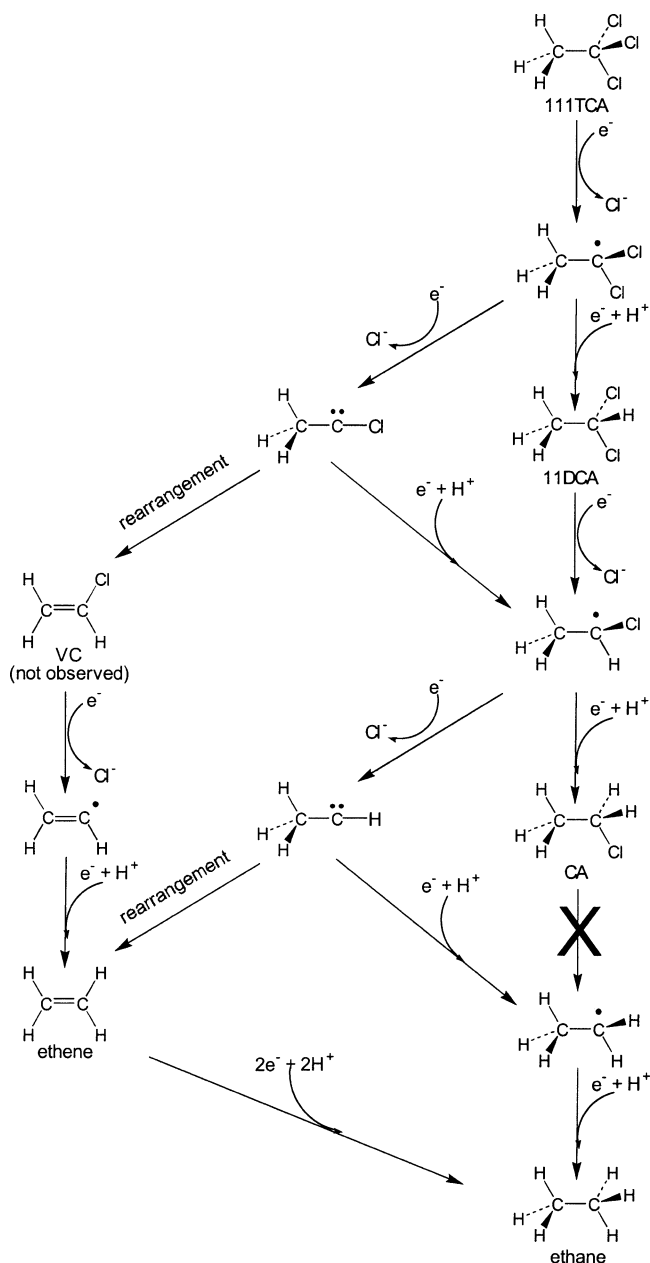
Fig. 2. Potential reaction scheme for the reduction of 1,1-dichloroethane (1,1-DCA) and 1,1,1-trichloroethane (1,1,1-TCA) to ethene and ethane. Chloroethane (CA) was not reduced, and vinyl chloride (VC) was not observed as an intermediate in the reduction of 1,1,1-TCA in our experimental systems.

Fig. 3. Proposed pathways for the reduction of chlorinated ethanes in aqueous green rust suspensions and in green rust suspensions spiked with Ag^I (AgGR) or Cu^{II} (CuGR); however, some elements of the pathways shown are not relevant to all experimental systems. Pathways leading to the formation of the C$_4$ hydrocarbons observed as products of the reduction of 1,1,1-trichloroethane (1,1,1-TCA) by AgGR or 1,1,2-trichloroethane (1,1,2-TCA) and pentachloroethane (PCA) by CuGR are not shown. HCA = hexachloroethane; 1,1,1,2-TeCA = 1,1,1,2-tetrachloroethane; 1,1,2,2-TeCA = 1,1,2,2-tetrachloroethane; 1,1-DCA = 1,1-dichloroethane; 1,2-DCA = 1,2-dichloroethane; CA = chloroethane; PCE = perchloroethene; TCE = trichloroethene; 1,1-DCE = 1,1-dichloroethene; *cis*-1,2-DCE = *cis*-1,2-dichloroethene; *trans*-1,2-DCE = *trans*-1,2-dichloroethene; VC = vinyl chloride; DCAc = dichloroacetylene; CAc = chloroacetylene; Ac = acetylene.

20 d, more than half the VC resulting from the reduction 1,1,2-TCA was further reduced to ethene and ethane in the presence of CuGR. Products resulting from the sequential hydrogenolysis of 1,1,2-TCA (i.e., 1,2-DCA, 1,1-DCA, and CA) were not observed in any of the experimental systems.

The reduction of 1,1,1-TCA was quite rapid. Levels of 1,1,1-TCA were reduced below detection limits within 16 min, 12 h, or 146 h in the presence of AgGR, CuGR, or green rust alone, respectively (Fig. 1). Chloroethane, 1,1-DCA, and ethane were the major products of the reduction of 1,1,1-TCA, along with lesser amounts of ethene and *n*-butane (Table 1). However, the C mass balance was incomplete in all three systems (with only 60–74% of the C added as 1,1,1-TCA being recovered as identified products), suggesting the formation of unidentified products. The distributions of products among the three experimental systems differed in that 1,1-DCA levels were lower in systems containing AgGR or CuGR, and *n*-butane was observed only in the presence of AgGR.

As with 1,1-DCA, the major products observed from 1,1,1-TCA reduction can be accounted for by a series of sequential hydrogenolysis reactions, such that 1,1,1-TCA → 1,1-DCA → CA → ethane. However, the kinetics of 1,1-DCA and CA reduction, observed independently, do not support such a reaction sequence. Specifically, CA is not reduced, and the kinetics of 1,1-DCA reduction do not account for the observed

tively (Fig. 1), whereas only 6% of 1,1,2-TCA was transformed after 49 d with green rust alone (Table 1). Vinyl chloride and 1,1-DCE were the major products of the reduction of 1,1,2-TCA by green rust alone, indicating dechlorination by both reductive β-elimination (resulting in VC) and dehydrohalogenation (resulting in 1,1-DCE) (Fig. 3). The trace amounts of ethene and ethane observed after 49 d suggest only minimal reduction of 1,1-DCE and VC by green rust during this interval. In the presence of AgGR or CuGR, 1,1,2-TCA was stoichiometrically reduced to VC by reductive β-elimination, but 1,1-DCE was not detected, suggesting that dehydrochlorination of 1,1,2-TCA was not significant in these systems. Vinyl chloride was not substantially reduced by AgGR; only trace levels of ethene and ethane were detected. However, after
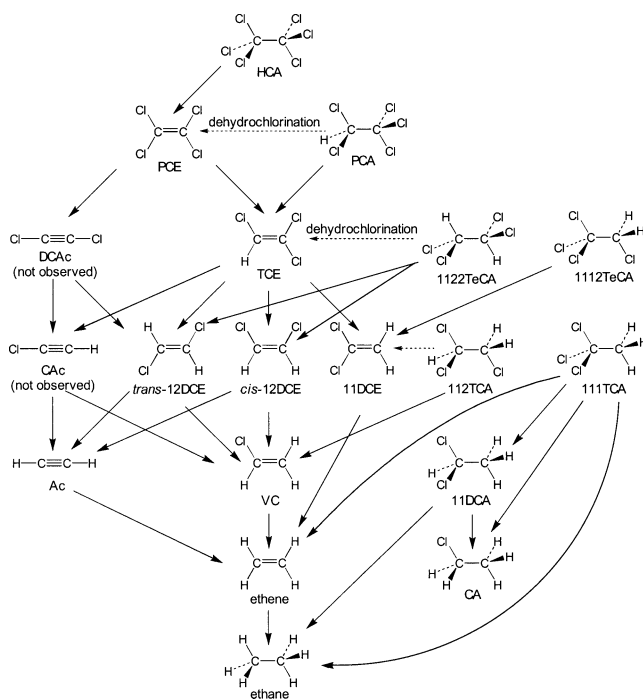
rates of CA and ethane accumulation. A reaction scheme consistent with the observed products and kinetics of 1,1,1-TCA reduction in our system is shown in Figure 2. For 1,1,1-TCA, a single electron transfer with the stepwise or concerted cleavage of a C–Cl bond results in the formation of a dichloroethane radical. The transfer of another electron and a proton to this radical forms 1,1-DCA, which can react further as described previously. Transfer of a single electron to the dichloroethane radical and loss of chloride results in chloroethanylidene (or its corresponding carbenoid). Rearrangement of chloroethanylidene yields VC, which is subsequently reduced to ethene and, ultimately, ethane. However, we did not observe VC during the reduction of 1,1,1-TCA, suggesting that this pathway is not significant. Alternatively, chloroethanylidene can accept an electron and a proton, thus forming a chloroethane radical. As discussed previously, the chloroethane radical might react further, forming CA or the corresponding carbene/carbenoid (which ultimately results in ethene and ethane). The reaction scheme depicted in Figure 2 is based primarily on a series of single electron transfers in which an α-haloethyl radical is reduced (with the loss of chloride) to the corresponding carbene. The carbene then undergoes rearrangement or is reduced (with a proton transfer) to an ethyl radical containing one less chlorine. If the radical is chlorinated, the cycle can continue. Castro and Kray [33] proposed this type of process to explain the kinetics and product distributions observed during the reduction of geminal halides (including 1,1,1-TCA) by Cr^{II} in aqueous solution. This reaction scheme was also invoked by Fennelly and Roberts [34] to explain the kinetics and product formation observed with the reduction of 1,1,1-TCA by Fe^0. The reaction scheme shown in Figure 2 does not depict reactions for the hydrolysis of chloroethanylidene and ethanylidene to, respectively, acetaldehyde and ethanol, which were not measured in our experiments.

In the presence of AgGR, *n*-butane was observed as a product of 1,1,1-TCA reduction (but not with CuGR or green rust alone), accounting for 9% of the C derived from 1,1,1-TCA; however, how the *n*-butane formed is not clear. The formation of *n*-butane was not observed during the reduction of 1,1-DCA (Table 1), suggesting that it is formed before or independent of the reduction of 1,1,1-TCA to 1,1-DCA. Fennelly and Roberts [34] suggested that the formation of 2-butyne and *cis*-2-butene observed during the reduction of 1,1,1-TCA by Fe^0 and Fe^0-containing bimetallic reductants is the result of the coupling of two dichloroethane radicals to form 2,2,3,3-tetrachlorobutane. After two successive β-elimination reactions, 2,2,3,3-tetrachlorobutane is reduced to 2-butyne, which can then be reduced to *cis*- and *trans*-2-butene. Although it was not observed by Fennelly and Roberts [34], *cis*-2-butene can be reduced to *n*-butane. The dichloroethane radical is an intermediate in the reaction scheme proposed for the reduction of 1,1,1-TCA by green rust (Fig. 2). However, the *n*-butane observed in our experiments is unlikely to have resulted from the coupling of dichloroethane radicals, because none of the intermediate products (2,2,3,3-tetrachlorobutane, *cis*- and *trans*-2,3-dichloro-2-butene, 2-butyne, or *cis*- and *trans*-2-butene) were observed in these experiments. Moreover, we did not observe the formation of any C_4 chlorinated hydrocarbons, thus precluding the formation of *n*-butane from the reduction of products of the coupling of chloroethanylidene or ethenyl radicals.

The reduction of 1,1,2,2-TeCA was complete in less than 1 or 49 h in the presence of AgGR or CuGR, respectively,

and after 560 h, 83% of the 1,1,2,2-TeCA was transformed by green rust alone (Fig. 1). Dehydrochlorination of 1,1,2,2-TeCA yields TCE, which was the dominant product of the transformation of 1,1,2,2-TeCA by green rust (Table 1). The minor amounts of *cis*-1,2-DCE and *trans*-1,2-DCE may have resulted from the reduction of TCE or from the reduction of 1,1,2,2-TeCA by β-elimination (Fig. 3). In contrast, relatively large levels of *cis*-1,2-DCE and *trans*-1,2-DCE were formed in the presence of AgGR or CuGR. Although *cis*-1,2-DCE and *trans*-1,2-DCE may be formed by the reduction of TCE (Fig. 3), the rapid appearance of the 1,2-DCE isomers relative to the slower accumulation of trace levels of TCE (with ≤1% of 1,1,2,2-TCA transformed to TCE) suggests that reductive β-elimination was the dominant reaction for the transformation of 1,1,2,2-TeCA in the presence of AgGR or CuGR. Little subsequent transformation of *cis*-1,2-DCE or *trans*-1,2-DCE by AgGR (with only trace levels of acetylene, ethene, and ethane) was observed; however, the accumulation of relatively high levels of ethene, along with lesser amounts of ethane and VC, indicates substantial reduction of *cis*-1,2-DCE and *trans*-1,2-DCE by CuGR (Fig. 3).

Green rust reduced 90% of added 1,1,1,2-TeCA after 560 h. However, AgGR or CuGR completely reduced 1,1,1,2-TeCA within 2 min or 1.5 h, respectively, which is significantly faster than 1,1,2,2-TeCA was reduced in these two systems (Fig. 1). In all three systems (i.e., AgGR, CuGR, and green rust alone), 1,1-DCE was the initial transformation product, indicating that reductive β-elimination was the initial reaction in the reduction of 1,1,1,2-TeCA; products resulting from hydrogenolysis (1,1,2-TCA or 1,1,1-TCA) and dehydrochlorination (TCE) were not observed at any time (Table 1). Although only minimal reduction of 1,1-DCE to VC, ethene, and ethane occurred with AgGR or green rust alone, substantial reduction of 1,1-DCE to ethene and ethane was observed with CuGR.

Complete transformation of PCA occurred within 21 h with green rust alone and within 2 or 48 min with AgGR or CuGR. Tetrachloroethene and TCE were the only products of PCA transformation by green rust (Table 1). The formation of PCE resulted from dehydrochlorination of PCA (Fig. 3). Although TCE may be formed by hydrogenolysis of PCE, the kinetics of TCE formation relative to PCE formation during the transformation of PCA suggest that the reduction of PCE to TCE was minimal; therefore, TCE was formed largely by reductive β-elimination of PCA. These results indicate that the dechlorination of PCA by green rust occurred by both dehydrochlorination and reductive β-elimination. However, in both metal-amended systems, the direct reduction of PCA to TCE by reductive β-elimination was the dominant reaction; only minor amounts of PCE were observed in the presence of AgGR or CuGR, indicating that dehydrochlorination was not a significant factor in the transformation of PCA in these systems. The PCE formed in the presence of AgGR was subsequently reduced to TCE, whereas in the CuGR system, the PCE that was formed was stable. Further reduction of PCA daughter products by AgGR was minimal; however, with CuGR, more than 50% of the PCA was reduced to nonchlorinated products (primarily ethene and ethane).

Hexachloroethane was reduced within 1 min, 45 min, or 8 h by AgGR, CuGR, or green rust, respectively (Fig. 1). In all three systems, HCA was reduced to PCE by reductive β-elimination; no evidence of PCA formation was observed, indicating that hydrogenolysis was not a significant reaction. No apparent reduction of PCE by green rust, and only minor re-

duction of PCE to TCE, ethene, and ethane by CuGR, was observed after 11 d (Table 1). However, within 11 d, PCE was completely reduced by AgGR, primarily to TCE. The formation of minor amounts of *cis*-1,2-DCE and *trans*-1,2-DCE is consistent with the reduction of TCE by hydrogenolysis. In addition, the significant amounts of acetylene observed could have been formed by the reduction of PCE by a number of routes (Fig. 3). Acetylene can be formed from *cis*-1,2-DCE and *trans*-1,2-DCE by reductive β-elimination, consistent with the formation of acetylene observed in the reduction of 1,1,2,2-TCA by AgGR (where *cis*-1,2-DCE and *trans*-1,2-DCE were the primary products). Acetylene can also be formed by the reductive dechlorination of dichloroacetylene and chloroacetylene, which are the products of the reductive β-elimination of PCE and TCE. Although dichloroacetylene and chloroacetylene were not observed directly as intermediates in the reduction of HCA by AgGR, they typically are highly reactive intermediates [35,36]; thus, they tend not to persist.

Comparison of AgGR and CuGR

Significant differences were observed in the rates of degradation (Fig. 1) and product distributions (Table 1) for halogenated ethanes reduced by AgGR or CuGR. As previously discussed, the rate of degradation of halogenated ethanes was consistently faster for AgGR than for CuGR. The same trend has been reported for the degradation of chlorinated methanes by AgGR or CuGR [26]. The reduction of halogenated ethanes by CuGR typically resulted in a greater yield of nonchlorinated products than that by AgGR. In addition, C_4 aliphatic hydrocarbons (mixtures of butane, *n*-butene, *cis*-2-butene, and *trans*-2-butene) were observed as trace products (≤1%) of the reduction of 1,1,1,2-TeCA, 1,1,2,2-TeCA, and PCA by CuGR, but these compounds were not products of corresponding reductions by AgGR. However, *n*-butane was a significant product of the reduction of 1,1,1-TCA by AgGR, although it was not observed with CuGR.

The differences in reaction rates and product distributions observed for AgGR and CuGR clearly result from the presence of silver and copper species in each of these systems. The addition of Ag^I or Cu^{II} to aqueous green rust suspensions results in the formation of submicron-sized particles of Ag^0 or Cu^0, respectively [21]. The association of Ag^0 or Cu^0 particles with green rust crystals may form galvanic cells wherein green rust serves as the anode (with oxidation of Fe^{II} to Fe^{III}) and Ag^0 or Cu^0 particles serve as the cathode (where the halogenated ethanes are reduced at the metal surface) [26]. If reduction of the halogenated ethanes is indeed occurring at the surface of Ag^0 or Cu^0, the differences in the surface atomic structures and electronic properties of these two metals are likely to affect the nature of the association of the parent compounds with the metal surfaces as well as the stability of reaction intermediates, contributing to the observed differences in reaction rates and product distributions.

Environmental relevance

The reduction of halogenated ethanes by green rust is relevant to understanding the processes relating to the long-term performance of zero-valent iron permeable reactive barriers (PRBs), the coupling of the microbial reduction of iron to contaminant reduction in the subsurface, and the development of innovative materials for remediation of halogenated hydrocarbon contamination.

Zero-valent iron has been the most extensively studied reductant for the treatment of chlorinated hydrocarbons and is currently the most commonly used material for the construction of PRBs [37]; however, a detailed understanding of the processes involved in the reduction of chlorinated hydrocarbons by metallic iron is lacking. This is particularly true regarding the role of Fe^{II} species in the reduction of chlorinated hydrocarbons in iron metal systems [38]. As described by Scherer et al. [38], the oxide layer formed by corrosion of the iron metal surface (resulting from reduction of water or chlorinated hydrocarbons) can act as a physical barrier, a semiconductor, or a reactive surface. Of the corrosion products identified in iron metal columns and barriers (including Fe^{II}-bearing minerals, such as magnetite, siderite, ferrous sulfide, and green rust, as well as Fe^{II} sorbed to mineral surfaces [39]), many have been shown to reduce chlorinated hydrocarbons. Our results showing the reduction of halogenated ethanes by green rust, along with previous studies of the reduction of chlorinated methanes and ethenes [7,18,26], suggest that these minerals may be useful for the remediation of halogenated hydrocarbon contaminants. Moreover, Williams and Scherer [16] suggested that the formation of Fe^{II}-bearing minerals, such as green rusts, partially explains the effectiveness of zero-valent iron PRBs over long time periods despite the formation of thick oxide films.

The role of microbial processes in the redox cycling of iron in the subsurface and the ways in which these processes can be coupled to contaminant remediation currently are active areas of research. Reduced Fe^{II} species can be formed in the subsurface by the metabolic activity of dissimilatory iron-reducing bacteria, a diverse group of bacteria that can couple the oxidation of organic compounds or hydrogen to Fe^{III} reduction. The reduction of Fe^{III} by dissimilatory iron-reducing bacteria results in the production of soluble Fe^{II} species, sorption of Fe^{II} to organic and inorganic phases, and formation of a host of Fe^{II}-bearing mineral phases, including green rusts, magnetite, siderite, vivianite, and ferruginous smectite [30,31,40]. Thus, stimulation of the activity of dissimilatory iron-reducing bacteria in the subsurface and subsequent formation of Fe^{II} species, including green rusts, might create an in situ PRB without excavation.

Use of green rusts as components in PRBs is not limited to biogenic green rust formed as a consequence of microbial iron reduction in the subsurface. Large quantities of green rust can be readily synthesized from relatively inexpensive commodity chemicals (e.g., ferrous sulfate [copperas] and sodium hydroxide [caustic soda]). Injection and dispersion of synthetic green rust suspensions into the subsurface may provide an easy, relatively inexpensive alternative to traditional zero-valent iron PRBs. In addition, the catalytic effect of specific transition metals on the reductive dehalogenation of halogenated hydrocarbons by green rust (as shown for Ag^I or Cu^{II} with halogenated ethanes in the present study as well as for Ag^I, Au^{III}, or Cu^{II} with CT and chloroform [26]), may prove to be useful in the development of improved materials for PRBs and other remediation technologies.

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